

# LEAD-FREE DEPOSITS FOR BEARING SURFACES

Patent number: WO9823444

Publication date: 1998-06-04

Inventor: BRASH WILLIAM; BROWN NEIL; NOBEL BENJAMIN;  
THOMSON DONALD; CHIRAFISI ANGELO

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US3787294  
US4994155

Applicant: LEARONAL INC (US)

Classification:

- International: B32B15/00; C25D3/30

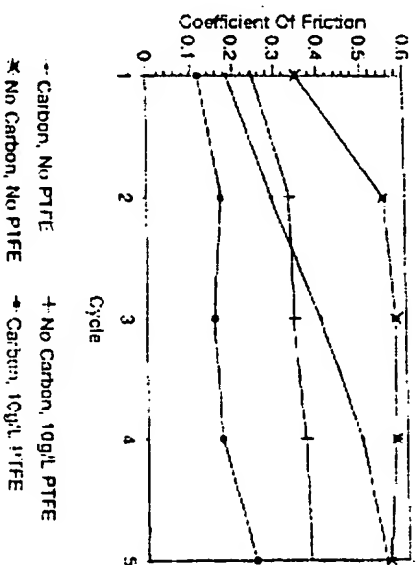
- European: C25D15/02

Application number: WO1997US21957 19971125

Priority number(s): US19960756504 19961126

## Abstract of WO9823444

A lead-free tin coating deposit for the contact surface for bearings or other frictional engagements, such as electrical connections, includes electrodeposited tin into which is incorporated a solid lubricant, such as powdered Teflon<TM>, graphite, and/or molybdenum disulfide, together with a small amount of codeposited carbon which generally is in the form of an organic compound or polymer. Optionally, additional alloying metals may also be provided in the coating deposit. An electroplating solution for depositing the tin, codeposited solid lubricant and codeposited carbon coating deposit is also provided. A method of electroplating a lead-free tin coating deposit having codeposited solid lubricant and codeposited carbon onto the contact surface of a bearing using the solution is also provided. Finally, a method of wetting PTFE powder to render it suitable for codeposition with tin as a coating deposit on the contact surface is provided.



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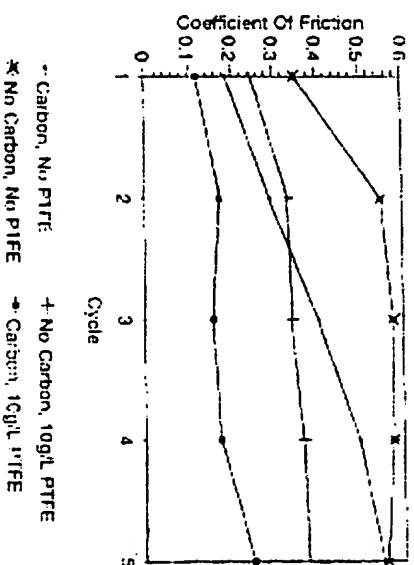
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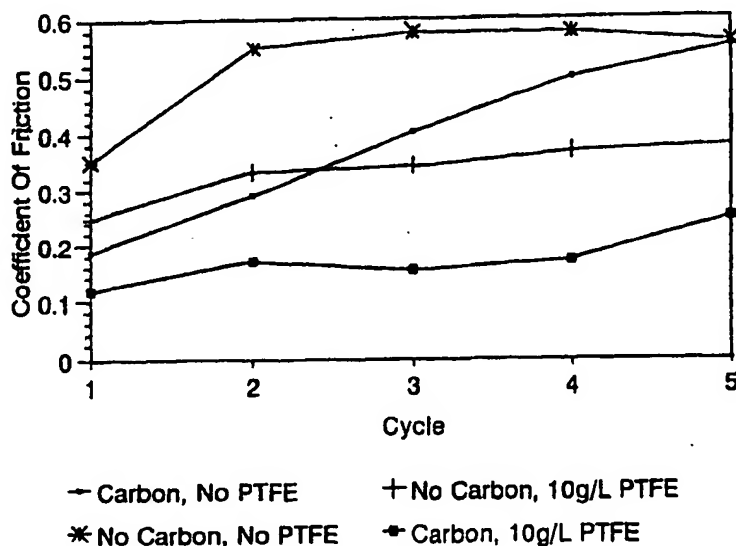






## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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			(43) International Publication Date: 4 June 1998 (04.06.98)
(21) International Application Number: <b>PCT/US97/21957</b> (22) International Filing Date: 25 November 1997 (25.11.97)  (30) Priority Data: 08/756,504                      26 November 1996 (26.11.96)      US  (71) Applicant: <b>LEARONAL, INC. [US/US]; 272 Buffalo Avenue, Freeport, NY 11520 (US).</b>  (72) Inventors: <b>THOMSON, Donald; 9 Gilder Court, Northport, NY 11768 (US). BRASH, William; 11 Canterbury Lane, Nesconset, NY 11767 (US). BROWN, Neil; 1787 Willis Avenue, Merrick, NY 11566 (US). CHIRAFISI, Angelo; 151-19 80th Street, Howard Beach, NY 11414 (US). NOBEL, Benjamin; 12A Plum Beach Point Road, Sands Point, NY 11050 (US).</b>  (74) Agent: <b>SIEGAL, Matthew, W.; Stroock &amp; Stroock &amp; Lavan LLP, 180 Maiden Lane, New York, NY 10038 (US).</b>		(81) Designated States: <b>BR, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b>  Published <i>With international search report.</i>	

(54) Title: **LEAD-FREE DEPOSITS FOR BEARING SURFACES**

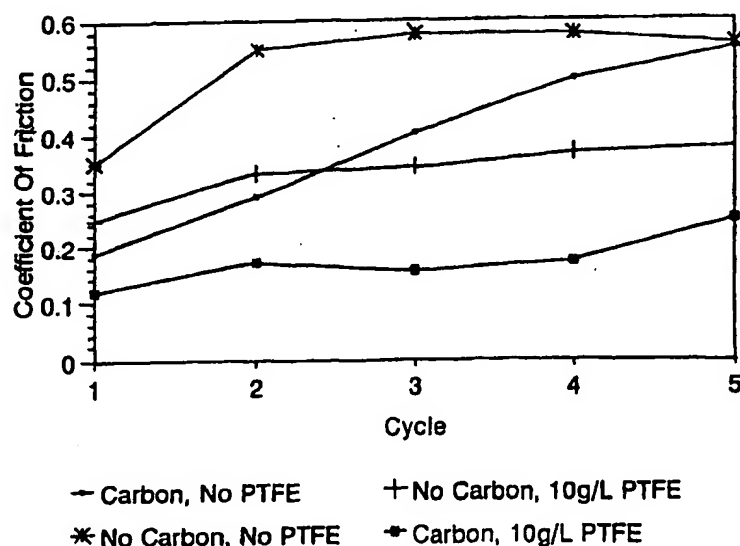
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## LEAD-FREE DEPOSITS FOR BEARING SURFACES

### BACKGROUND OF THE INVENTION

This invention relates generally to lead free surface coatings for bearings and more particularly to electrodeposits used as a contact surface on bearings and other surfaces in frictional engagement, and to electrodeposit bath solutions and  
5 systems for applying such deposits, particularly deposits containing no, or significantly reduced lead, and exhibiting a low friction coefficient and good resistance to wear.

A bearing is a component of a mechanical device that is in sliding or rolling contact with a corresponding mating component of the mechanical device.  
10 Typically, bearings may be gears, shafts, sleeves, piston rings, machine slideways or balls. The outer portion of the bearing that takes part in the rolling or sliding contact may be termed the contact surface of the bearing. The contact surface is typically composed of a material that has a low coefficient of friction and a low rate of wear.

Bearings for use in automotive engines and heavy machinery are  
15 generally made from steel or alloy steels. The contact surfaces of these and other heavy-duty bearings are typically coated with a high lead alloy deposited coating which provides the low friction and wearability suitable for such applications. The lead alloy coating is typically applied by electrodeposition and is frequently an alloy composition containing 88% lead, 10% tin, and 2% copper. For many years, the  
20 above described alloy has been an acceptable contact finish for bearings, and indeed, is a preferred contact finish for many heavy-duty use bearings.

There is presently a strong interest in eliminating hazardous materials from the work environment. Therefore, a suitable lead-free contact surface coating for bearings, or one having significantly lower lead content, yet still having the wear,  
25 adherence and friction properties to function as a bearing surface is very desirable. However, to date, it has not been satisfactorily realized.

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A large number of solid lubricants such as Teflon®, a polytetrafluoroethylene (PTFE) material sold by DuPont, graphite, molybdenum disulfide and others have been in use for many years. Attempts have been made in the prior art to incorporate these and other solid lubricants into surfaces for a wide variety of purposes with varying degrees of success. For example, Japanese Patent publication JP 95-36097 discloses a sintered tin-teflon coating for copying machine fixing rollers. Pocock et al, Wear 37 129-41 (1976) discloses that a high temperature reaction catalyzed by copper occurs between tin and PTFE, and suggests that this reaction is useful for bonding PTFE to a bearing surface.

U.S. Patent 3,674,689 describes a bearing component whose contact surface is a composite synthetic resin matrix having metal coated carbon fibers incorporated within, and used for reinforcement.

E. Steiger et al, Galvanotechnik 81 (1990) 443-447 describes an electroless nickel deposition process which incorporates PTFE, graphite powder, or molybdenum disulfide into the nickel surface. V. Bhalla et al., Plating and Surface Finishing, November (1995) 58-61 describe surfaces having PTFE powder, graphite, or molybdenum disulfide electrocodeposited with copper. M. Ghouse, Metal Finishing, November (1980) 55-60 describes electrocodeposited copper surfaces having inclusions of graphite, molybdenum disulfide, and tungsten disulfide for tribological applications. M. Ghouse et al, Metal Finishing, June (1981) 85-89 discloses electrocodeposited copper surfaces having inclusions of graphite and molybdenum disulfide.

Transactions of IMF (1996) 7499-102 describes electroless nickel-copper-phosphorous alloys having inclusions of PTFE powder for improved tribological properties.

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substrate is immersed into a plating bath containing platinum and PTFE. By reversing the polarity of the substrate at 10 - 60 second intervals, alternate layers of platinum and PTFE are deposited. The contents of this patent is incorporated herein by reference.

5 U.S. Patent No. 3,434,942 describes electrodeposition of lead and PTFE. In one example, a steel strip is coated with a cladding layer of 80% copper, 10% lead and 10% tin. The strip is first plated with lead and then PTFE is deposited thereon from an electrophoresis cell. The addition of graphite or molybdenum disulfide onto the lead surface is also described. The contents of this patent are also incorporated  
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British Patent 1,366,823 describes a process for codepositing organic particles with various metals. The process involves electrodepositing a film from a  
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However, regardless of the foregoing processes which relate to various fields, a plated surface, plating bath and plating method for providing a low friction  
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### SUMMARY OF THE INVENTION

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Accordingly, it is an object of the invention to provide an improved lead-free coating deposit for a contact surface of a bearing.

Another object of the invention is to provide an improved electroplating solution for electrolytically depositing a lead-free coating deposit onto, for example, the contact surface of a bearing.

A further object of the invention is to provide a method of electroplating a lead-free coating deposit onto a contact surface of a bearing.

Still a further object of the invention is to provide a method of rendering PTFE powder suitable for codeposition with metals by dispersing the PTFE within the electroplating solution.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification and drawings.

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the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

5           For a fuller understanding of the invention, reference is had to the following description, taken in connection with the accompanying drawings, in which:

Fig. 1 is a graph showing the results of a test for measuring the coefficient of friction of various contact surfaces of bearings, including contact surfaces of the invention using PTFE as a solid lubricant;

10           Fig. 2 is a graph showing the results of a test for measuring the coefficient of friction of various contact surfaces of bearings made in accordance with the invention in which different acids are used in the electroplating bath;

Fig. 3 is a graph showing the results of a test for measuring the coefficient of friction of various contact surfaces of bearings made in accordance with the invention in which different solid lubricants are included in the electroplating bath;

15           Fig. 4 is a graph showing the results of a test for measuring the coefficient of friction of various contact surfaces of bearings, including contact surfaces of the invention using molybdenum disulfide as a solid lubricant;

Fig. 5 is a graph showing the results of a test for measuring the coefficient of friction of various contact surfaces of bearings, including contact surfaces of the invention using graphite as a solid lubricant; and

20           Fig. 6 is a graph showing the results of a test for measuring the coefficient of friction of various contact surfaces of bearings, including contact surfaces of the invention using different amount of PTFE as a solid lubricant.

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20           coefficient of friction of various contact surfaces of bearings, including contact surfaces of the invention using graphite as a solid lubricant; and

          Fig. 6 is a graph showing the results of a test for measuring the coefficient of friction of various contact surfaces of bearings, including contact surfaces of the invention using different amount of PTFE as a solid lubricant.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It is desirable to prepare lead-free or substantially lead-free bearing surfaces which have the same or better friction and/or wear properties as conventional surfaces including lead. The preferred lead-free coating should have the same or similar properties as the present high-lead alloy 88:10:2 lead:tin:copper bearing contact surface coatings, such as (1) good lubricity, (2) low friction, (3) softness to readily conform to the mating surface, (4) ability to easily absorb fine particles which may form from normal wear as the bearing is used, and (5) low rate of wear.

To accomplish the foregoing, it has been determined that it is desirable to include a solid lubricant in a metal coating, said metal consisting of or having a high content of tin. It has also been determined that solid lubricants, such as polytetrafluoroethylene (PTFE or "teflon"), molybdenum disulfide and graphite are suitable as the solid lubricant when incorporated into a tin surface, preferably along with carbon from organic molecules or polymers, and/or an alloying metal.

Tin can be electroplated from acid plating solutions. To optimize the properties of the plated surface, these plating solutions should also contain certain compatible soluble surface active agents which act as grain refiners and brighteners. Examples of acids which may be used in electroplating solutions with tin in accordance with the invention include sulfuric acid, sulfamic acid, fluoboric acid, and methanesulfonic acid (MSA). Tin can be added to the electroplating bath as a soluble divalent compound, preferably as the salt of the particular acid to be used, such as, for example, tin sulfate with sulfuric acid, tin fluoborate with fluoboric acid, and tin methanesulfonate with MSA. The acid is included in a concentration to keep the tin in a soluble state. The plating solution can also contain various other additives commonly used in plating processes, such as antioxidants, as set forth in U.S. Pat. No. 5,066,367, the contents of which are incorporated herein by reference.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It is desirable to prepare lead-free or substantially lead-free bearing surfaces which have the same or better friction and/or wear properties as conventional surfaces including lead. The preferred lead-free coating should have the same or similar properties as the present high-lead alloy 88:10:2 lead:tin:copper bearing contact surface coatings, such as (1) good lubricity, (2) low friction, (3) softness to readily conform to the mating surface, (4) ability to easily absorb fine particles which may form from normal wear as the bearing is used, and (5) low rate of wear.

To accomplish the foregoing, it has been determined that it is desirable to include a solid lubricant in a metal coating, said metal consisting of or having a high content of tin. It has also been determined that solid lubricants, such as polytetrafluoroethylene (PTFE or "teflon"), molybdenum disulfide and graphite are suitable as the solid lubricant when incorporated into a tin surface, preferably along with carbon from organic molecules or polymers, and/or an alloying metal.

Tin can be electroplated from acid plating solutions. To optimize the properties of the plated surface, these plating solutions should also contain certain compatible soluble surface active agents which act as grain refiners and brighteners. Examples of acids which may be used in electroplating solutions with tin in accordance with the invention include sulfuric acid, sulfamic acid, fluoboric acid, and methanesulfonic acid (MSA). Tin can be added to the electroplating bath as a soluble divalent compound, preferably as the salt of the particular acid to be used, such as, for example, tin sulfate with sulfuric acid, tin fluoborate with fluoboric acid, and tin methanesulfonate with MSA. The acid is included in a concentration to keep the tin in a soluble state. The plating solution can also contain various other additives commonly used in plating processes, such as antioxidants, as set forth in U.S. Pat. No. 5,066,367, the contents of which are incorporated herein by reference.

Many compatible surface-active agents can be used as additives to improve the deposit characteristics of the tin. They include those set forth in U.S. Patent No. 4,565,610, U.S. Patent No. 4,459,185, U.S. Patent No. 4,923,576, U.S. Patent No. 5,282,953, and U.S. Patent No. 5,282,954. The contents of these patents  
5 are incorporated herein by reference. The surface active agents described in these references are of generally at least one or more of the following classes:

a. Non-ionic surfactants containing higher alcohols condensed with alkylene oxide groups. The alkylene oxides may be selected from among, for example, ethylene oxide, propylene oxide and combinations thereof. The higher  
10 alcohols may be selected from among, for example, aliphatic alcohols, aromatic alcohols, heterocyclic alcohols and combinations thereof.

b. Surfactants as in (a) in which the terminal hydroxide group has been modified to include a solubilizing group which may be selected from among, for example, a halide, an amine, a sulfate, a sulfonate, a phosphate, a phosphonate and  
15 combinations thereof. These solubilizing groups tend to change the non-ionic nature of a surfactant to either anionic or cationic, depending on the nature of the group added.

c. Amphoteric surfactants, which may be selected from, for example, betaines, sulfobetaines, sulfated or sulfonated adducts of organic amines condensed  
20 with alkylene oxides, imidazoline compounds and combinations thereof.

d. Cationic surfactants, which may be selected from, for example, higher organic amine salts, quaternaryammonium salts, amine oxides and combinations thereof.

e. Anionic surfactants, which may be selected from, for example, higher  
25 organic sulfonates, higher organic sulfates and combinations thereof.

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25 organic sulfonates, higher organic sulfates and combinations thereof.

It has been found that the surfactants which are particularly useful for this invention are those that both produce fine grained tin deposits and also incorporate a small amount of carbon by codeposition into the deposit. The codeposited carbon is typically in the form of an organic compound or polymer. Carbon can also be  
5 incorporated by codeposition into the tin deposits by adding brightening agents which produce bright tin deposits. These brighteners include, for example, formaldehyde, lower aliphatic aldehydes, aromatic aldehydes, heterocyclic aldehydes and combinations thereof.

The quantity of codeposited carbon may be accurately determined by a  
10 laboratory that specializes in this type of quantitative analysis, for example, Leco Corporation in St. Joseph, Michigan. The carbon is burned off at relatively low temperatures and measured by measuring the amount of  $\text{CO}_2$  which comes off.

It has been found that additives in a plating bath that act as brighteners and/or cause grain refinement will codeposit a carbon-containing compound or  
15 polymer with the metal being plated. It is believed that these carbon compounds deposit at the metal grain boundary and inhibit grain growth and promote smooth, fine-grained tin deposits. The quantity of codeposited carbon can be analyzed readily, and is considered to be a measure of the amount of codeposited compound or polymer. An extensive discussion of codeposited organic compounds with gold is presented by  
20 G. B. Munier in Plating, October 1969, 1151-1157, which is incorporated herein by reference.

The organic compounds codeposited with tin can also affect other properties of the deposited tin, such as, for example, solderability and are generally believed to be undesirable. Conventional processes generally seek to keep these at a  
25 minimum and have not recognized the benefits in lowered friction coefficient resulting from codeposited compounds from these grain refiners and brighteners. For example,

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Military Specification MIL-M-38501 H limits the amount of carbon codeposited with tin to a maximum of 0.05% by weight and does not distinguish between sources of such carbon which provide benefits and those which do not. An extensive discussion of codeposited organic compounds and carbon with tin was given by J. L. Martin and  
5 M. P. Toben at a conference of the American Electroplaters and Surface Finishers Society, AESF SUR/FIN Technical Conference Proceedings, June 1988, the contents of which are incorporated herein by reference.

In accordance with the invention, powdered PTFE, graphite, and molybdenum disulfide lubricant can be codeposited with tin by previously wetting the  
10 powder, then adding the wetted slurry to the plating bath. Powdered graphite and molybdenum disulfide can be wetted by water and the slurry added directly to the tin plating solution. PTFE powder, however, presents a special problem, since it is generally considered to be non-wettable. It was surprisingly found that powdered PTFE could be wetted by first mixing the powder with a water soluble solvent, such as  
15 acetone, methanol or isopropyl alcohol, for example, and adding a small amount of surfactant, such as a non-ionic, anionic or amphoteric surfactant. This slurry mixture may then be added to the tin plating solution to incorporate teflon powder into the deposit. A preferred mixture to make PTFE powder wettable is a mixture of acetone and a non-ionic surfactant, such as, for example, nonylphenol ethoxylate.

20 The plating bath is stirred or agitated during the plating process to keep the solid lubricant powder distributed evenly without settling out on the bottom of the plating vessel. During the plating process, some of the powder will codeposit with the tin by its physical presence at the surface of the component being plated. The amount of PTFE thus codeposited can be determined by melting the tin deposit. The melted  
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25 tin coating ejects the powder and the amount of codeposited PTFE powder is thus

determined by a weight-difference of the tin deposit before and after melting. The amount of tin in the plated surface is generally greater than 99%.

In order to determine the coefficient of friction of tin deposits, both with and without codeposited solid lubricants, and both with and without codeposited carbon, the following procedure was used. Tin, or tin and codeposited components were initially deposited onto the contact surface of a brass or steel coupon and this coupon is placed into a testing apparatus. A nickel plated brass hemispherical rider is made to ride back and forth on the tin surface and the horizontal force needed to move the rider is measured accurately with a strain gage. Measurements were made on five complete back and forth cycles. The coefficient of friction is calculated from this horizontal force and the vertical force contributed by the weight of the rider. The coefficient of friction is used as a comparative measure of the suitability of any given contact surface.

It has been found that the coefficient of friction of tin deposits is reduced when a solid lubricant such as teflon is incorporated into the tin deposits. However, surprisingly, the coefficient of friction is markedly reduced further when the tin deposit also includes codeposited carbon from appropriate sources, as described above, along with the codeposited lubricant. The codeposition of carbon as an organic compound or polymer also significantly lowers the coefficient of friction of a tin surface when codeposited with graphite or molybdenum disulfide.

It is the combination of both codeposited carbon and codeposited PTFE that imparts the lowest coefficient of friction to the tin deposits, and which make them particularly advantageous as a contact surface. Similar results are achieved with a combination of codeposited graphite and codeposited carbon along with tin, and also with codeposited molybdenum disulfide and carbon along with tin.

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Although the above discussion is given in terms of codeposited carbon plus a codeposited friction reducing solid lubricant powder along with electro-deposited pure tin, it should be recognized that small amounts of traditional alloying elements can also advantageously be added in appropriate ranges. Thus, the invention  
5 herein described is not limited to pure tin alone. For example, copper can be included as an alloying element to add hardness to the deposited contact surface if needed. Likewise, bismuth may be added to reduce the melting point or to help prevent tin "pest" or tin "disease". Other alloying ingredients, including lead, which is particularly useful as an alloying element to prevent "whisker" growth in tin deposits  
10 and is useful in coating plug-in type electrical contact pins and the like, known in the art. If copper is added, the plated surface should have about 1-5% copper. If lead is added, the plated surface should include more than about 1% lead, preferably about 5-10% lead. If bismuth is added to suppress tin pest, the surface should include at least about 0.3%, preferably about 1% bismuth.

15 When preparing a plating bath, the following components should be added in the following proportions.

Teflon (PTFE) should be included so as to lower the coefficient of friction of the plated surface without adversely affecting the wear resistance of the surface. Suitable proportions for the bath are in a range of about 1 g/l to about 30 g/l  
20 preferably about 5g/l to about 20 g/l and most preferably about 10 g/l to about 15 g/l. Suitable particle sizes for PTFE range from about 0.05 micron to about 10 micron, preferably about 0.1 micron to about 0.3 micron.

Graphite is advantageously included to lower the coefficient of friction in the plated surface without adversely affecting the wear resistance in a range of  
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25 about 1 g/l to about 30 g/l, preferably about 5 g/l to about 20 g/l, and most preferably

about 10 g/l to about 15 g/l. Suitable particle sizes for graphite range from about 0.05 micron to about 10 micron preferably about 1 micron to about 2 micron.

Molybdenum disulfide should be included to lower the coefficient of friction without adversely affecting the wear resistance in a range of about 1 g/l to about 30 g/l, preferably about 5 g/l to about 20 g/l, and most preferably about 10 g/l to about 15 g/l. Suitable particle sizes for molybdenum disulfide range from about 0.05 micron to about 10 micron, preferably about 0.1 micron to about 0.5 micron.

The carbon source additive is preferably added to the plating bath in an amount to decrease the frictional coefficient of the plated surface. The additive may be added in a range of about 0.05 g/l to about 10 g/l, preferably about 0.5 g/l to about 5 g/l. Although lesser amounts can be used, amounts greater than about 1 g/l and often 2 g/l of certain materials such as bisphenol A ethoxylate and like substances are well suited for lowering the coefficient of friction of a surface with codeposited solid lubricant.

The scope of the invention is further described in connection with the following examples, which are set forth for the purpose of illustrating preferred embodiments of the invention only and are not to be construed as limiting the scope of the invention in any manner. It should be noted that various known commercially used plating additives, such as anti-oxidants which can keep <sup>+2</sup> tin from becoming <sup>+4</sup> tin and other additives which do not significantly affect the performance of the invention can be used. A hydroxy phenyl anti-oxidant as disclosed in U.S. Patent No. 5,066,367 for preventing <sup>+2</sup> Sn from being oxidized to <sup>+4</sup> Sn was used in Example 5.

Example 1 (For comparison)

Tin Metal as Tin Sulfate	15 g/l
Sulfuric Acid	100 ml/l

about 10 g/l to about 15 g/l. Suitable particle sizes for graphite range from about 0.05 micron to about 10 micron preferably about 1 micron to about 2 micron.

Molybdenum disulfide should be included to lower the coefficient of friction without adversely affecting the wear resistance in a range of about 1 g/l to about 30 g/l, preferably about 5 g/l to about 20 g/l, and most preferably about 10 g/l to about 15 g/l. Suitable particle sizes for molybdenum disulfide range from about 0.05 micron to about 10 micron, preferably about 0.1 micron to about 0.5 micron.

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Example 1 (For comparison)

Tin Metal as Tin Sulfate	15 g/l
Sulfuric Acid	100 ml/l



	Temperature	Room
	Agitation	Mild
	Current Density	20 ASF
	Time	15 minutes
5	Plating Thickness	0.0005 in.

This tin deposit contained no codeposited teflon, and no codeposited carbon.

#### Example 2 (PTFE Alone)

Ten (10) grams of MP1000 PTFE powder, a DuPont Teflon product,  
10 was mixed with 500 ml acetone until all of the PTFE powder was wetted and the slurry was added to the bath of Example 1. No surfactant was added in this Example. Thus, there was obtained a coarser grained tin-teflon deposit coating with no co-deposited carbon from a surfactant or additive. The large amount of acetone was needed in this experiment to keep the teflon powder sufficiently wet.

#### 15 Example 3 (Carbon Source Alone)

To the bath of Example 1, add 0.1 g/l nonylphenol ethoxylated with 12  
mols ethylene oxide and 4 g/l ethoxylated bisphenol A with 12 mols ethylene oxide. The deposited coating contained codeposited carbon in the form of an organic polymer but no codeposited teflon. The carbon content of the tin coating deposited in this  
20 example was found to be 0.003%.

#### Example 4 (PTFE and Carbon Source)

To the bath of Example 3, add 10 g/l PTFE powder previously wetted with 20 ml acetone and 0.1 g ethoxylated nonylphenol. This tin coating contained both carbon and teflon codeposited along with the tin. Note, the codeposited teflon in

Temperature	Room
Agitation	Mild
Current Density	20 ASF
Time	15 minutes
5 Plating Thickness	0.0005 in.

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#### Example 2 (PTFE Alone)

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20 example was found to be 0.003%.

#### Example 4 (PTFE and Carbon Source)

To the bath of Example 3, add 10 g/l PTFE powder previously wetted with 20 ml acetone and 0.1 g ethoxylated nonylphenol. This tin coating contained both carbon and teflon codeposited along with the tin. Note, the codeposited teflon in

this example also tended to add a small amount of carbon to the deposited coating because carbon is part of the PTFE molecule. This added carbon is not considered and is not to be confused with carbon codeposited from the surfactants added in Example 3.

5           Each of the above electrolytic bath solutions (Examples 1 - 4) were used to coat a metal coupon and the coefficient of friction of the coated coupon was measured as described above. The results of the measured coefficients of friction for Examples 1 - 4 are presented in Fig. 1.

10           Example 4 resulted in the greatest decrease of frictional coefficient, thus demonstrating that the codeposited teflon and codeposited carbon from organic polymer combined to lower friction better than any other test result.

Example 5 (Methane Sulfonic Acid Bath (MSA), Teflon and Carbon Source)

	Tin as Tin MSA	15 g/l
15	MSA	150 ml/l
	Teflon Powder	10 g/l
	Acetone	20 ml/l
	Nonyl Phenol Ethoxylate	0.1 g/l
	Bisphenol A Ethoxylate	4 g/l
20	Temperature	110°F
	Current Density	20 ASF
	Time	15 minutes
	Agitation	Mild

this example also tended to add a small amount of carbon to the deposited coating because carbon is part of the PTFE molecule. This added carbon is not considered and is not to be confused with carbon codeposited from the surfactants added in Example 3.

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Example 5 (Methane Sulfonic Acid Bath (MSA), Teflon and Carbon Source)

	Tin as Tin MSA	15 g/l
15	MSA	150 ml/l
	Teflon Powder	10 g/l
	Acetone	20 ml/l
	Nonyl Phenol Ethoxylate	0.1 g/l
	Bisphenol A Ethoxylate	4 g/l
20	Temperature	110°F
	Current Density	20 ASF
	Time	15 minutes
	Agitation	Mild

Example 6 (Fluoboric Acid Bath, Teflon and Carbon Source)

	Tin as Tin Fluoborate	15 g/l
	Fluoboric Acid	164 ml/l
	Teflon Powder	10 g/l
5	Acetone	20 ml/l
	Nonyl Phenol Ethoxylate	0.1 g/l
	Bisphenol A Ethoxylate	4 g/l

Plating conditions as in example 5, above.

Example 7 (Sulfuric Acid Bath, Teflon and Carbon Source)

10	Tin as Tin Sulfate	15 g/l
	Sulfuric Acid	100 ml/l
	Teflon Powder	10 g/l
	Acetone	20 ml/l
	Nonyl Phenol Ethoxylate	0.1 g/l
15	Bisphenol A Ethoxylate	4 g/l

Plating conditions as in example 5 above.

Each of the above electrolytic bath solutions of Examples 5 - 7 were used to coat a coupon and the coefficient of friction of the coated coupon was measured as described above. The results of the measured coefficients of friction for  
20 Examples 5 - 7 are presented in Fig. 2.

The MSA-based solution gave the best results for reducing the coefficient of friction. However, the sulfuric and fluoboric acid based solutions with

Example 6 (Fluoboric Acid Bath, Teflon and Carbon Source)

	Tin as Tin Fluoborate	15 g/l
	Fluoboric Acid	164 ml/l
	Teflon Powder	10 g/l
5	Acetone	20 ml/l
	Nonyl Phenol Ethoxylate	0.1 g/l
	Bisphenol A Ethoxylate	4 g/l

Plating conditions as in example 5, above.

Example 7 (Sulfuric Acid Bath, Teflon and Carbon Source)

10	Tin as Tin Sulfate	15 g/l
	Sulfuric Acid	100 ml/l
	Teflon Powder	10 g/l
	Acetone	20 ml/l
	Nonyl Phenol Ethoxylate	0.1 g/l
15	Bisphenol A Ethoxylate	4 g/l

Plating conditions as in example 5 above.

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The MSA-based solution gave the best results for reducing the coefficient of friction. However, the sulfuric and fluoboric acid based solutions with

the tin, codeposited teflon and codeposited carbon coating deposits performed very well and are also an improvement over the coating deposits shown by the results of Examples 1, 2, and 3.

Example 8 (Teflon and Carbon Source)

5	Tin as Tin Sulfate	15 g/l
	Sulfuric Acid	100 ml/l
	Teflon Powder	10 g/l
	Acetone	20 ml/l
	Nonyl Phenol Ethoxylate	0.1 g/l
10	Bisphenol A Ethoxylate	4 g/l
	Current Density	20 ASF
	Temperature	Room
	Time	15 minutes
	Agitation	Mild

15 Example 9 (Molybdenum Disulfide and Carbon Source)

Ten (10) g/l molybdenum disulfide powder was used in place of 10 g/l teflon powder of Example 8 and acetone was not used.

Example 10 (Graphite and Carbon Source)

20 Ten (10) g/l graphite powder was used in place of 10 g/l teflon powder of Example 8 and acetone was not used.

Each of the above electrolytic bath solutions of Examples 8 - 10 were used to coat a coupon and the coefficient of friction of the coated coupon was

the tin, codeposited teflon and codeposited carbon coating deposits performed very well and are also an improvement over the coating deposits shown by the results of Examples 1, 2, and 3.

Example 8 (Teflon and Carbon Source)

5	Tin as Tin Sulfate	15 g/l
	Sulfuric Acid	100 ml/l
	Teflon Powder	10 g/l
	Acetone	20 ml/l
	Nonyl Phenol Ethoxylate	0.1 g/l
10	Bisphenol A Ethoxylate	4 g/l
	Current Density	20 ASF
	Temperature	Room
	Time	15 minutes
	Agitation	Mild

15 Example 9 (Molybdenum Disulfide and Carbon Source)

Ten (10) g/l molybdenum disulfide powder was used in place of 10 g/l teflon powder of Example 8 and acetone was not used.

Example 10 (Graphite and Carbon Source)

20 Ten (10) g/l graphite powder was used in place of 10 g/l teflon powder of Example 8 and acetone was not used.

Each of the above electrolytic bath solutions of Examples 8 - 10 were used to coat a coupon and the coefficient of friction of the coated coupon was



measured as described above. The results of the measured coefficients of friction for Examples 8 - 10 are presented in Fig. 3.

As shown by Figure 3, codeposited graphite plus codeposited carbon, and codeposited molybdenum disulfide plus codeposited carbon also give highly suitable results in terms of reducing friction when used as a coating deposit for a bearing.

Example 11 (Graphite, No Carbon Source)

	Tin metal as Tin Sulfate	15 g/l
	Sulfuric Acid	100 ml/l
10	Graphite Powder	10 g/l
	Current Density	20 ASF
	Temperature	Room
	Time	15 minutes
	Agitation	Mild

15 This tin deposit included codeposited graphite but no codeposited carbon from added surfactant or other additives.

Example 12 (Molybdenum Disulfide, No Carbon Source)

Metal was deposited as in example 11, except that 10 g/l molybdenum disulfide was substituted in place of graphite.

20 This tin deposit included codeposited molybdenum disulfide but no codeposited carbon from added surfactant or other additives.

Each of the above electrolytic bath solutions of Examples 11 and 12 were used to coat a coupon and the coefficient of friction of the coated coupon was

measured as described above. The results of the measured coefficients of friction for Examples 8 - 10 are presented in Fig. 3.

As shown by Figure 3, codeposited graphite plus codeposited carbon, and codeposited molybdenum disulfide plus codeposited carbon also give highly suitable results in terms of reducing friction when used as a coating deposit for a bearing.

Example 11 (Graphite, No Carbon Source)

	Tin metal as Tin Sulfate	15 g/l
	Sulfuric Acid	100 ml/l
10	Graphite Powder	10 g/l
	Current Density	20 ASF
	Temperature	Room
	Time	15 minutes
	Agitation	Mild

15 This tin deposit included codeposited graphite but no codeposited carbon from added surfactant or other additives.

Example 12 (Molybdenum Disulfide, No Carbon Source)

Metal was deposited as in example 11, except that 10 g/l molybdenum disulfide was substituted in place of graphite.

20 This tin deposit included codeposited molybdenum disulfide but no codeposited carbon from added surfactant or other additives.

Each of the above electrolytic bath solutions of Examples 11 and 12 were used to coat a coupon and the coefficient of friction of the coated coupon was

measured as described above. The results of the measured coefficients of friction for Examples 11 - 12 are presented in Figs. 4 and 5.

As shown by Figs. 4 and 5, there is a reduction of frictional coefficient caused by including codeposited carbon from surfactants or other additives together with codeposited graphite or codeposited molybdenum disulfide. Figs. 1, 4, and 5 show that tin-carbon-teflon, tin-carbon-graphite, and tin-carbon molybdenum disulfide, give significantly lower friction coefficients than their counterparts that do not contain codeposited carbon from added surfactant or other additives.

Example 13 (Water Soluble Solvents for Wetting PTFE Powder)

To demonstrate methods for wetting teflon powder, three separate mixtures (a - c) were prepared:

10	a)	Teflon powder	10 g
		Acetone	20 ml
		Nonylphenol Ethoxylate	0.1 g
15	b)	Teflon powder	10 g
		Isopropanol	20 ml
		Nonylphenol Ethoxylate	0.1 g
20	c)	Teflon powder	10 g
		Methanol	20 ml
		Nonylphenol Ethoxylate	0.1 g

Each mixture was stirred to wet the teflon powder, then each added separately to one liter of the solution of Example 3. The results indicate that in each

measured as described above. The results of the measured coefficients of friction for Examples 11 - 12 are presented in Figs. 4 and 5.

As shown by Figs. 4 and 5, there is a reduction of frictional coefficient caused by including codeposited carbon from surfactants or other additives together with codeposited graphite or codeposited molybdenum disulfide. Figs. 1, 4, and 5 show that tin-carbon-teflon, tin-carbon-graphite, and tin-carbon molybdenum disulfide, give significantly lower friction coefficients than their counterparts that do not contain codeposited carbon from added surfactant or other additives.

Example 13 (Water Soluble Solvents for Wetting PTFE Powder)

To demonstrate methods for wetting teflon powder, three separate mixtures (a - c) were prepared:

	a)	Teflon powder	10 g
		Acetone	20 ml
		Nonylphenol Ethoxylate	0.1 g
15	b)	Teflon powder	10 g
		Isopropanol	20 ml
		Nonylphenol Ethoxylate	0.1 g
	c)	Teflon powder	10 g
		Methanol	20 ml
20		Nonylphenol Ethoxylate	0.1 g

Each mixture was stirred to wet the teflon powder, then each added separately to one liter of the solution of Example 3. The results indicate that in each

solvent, the teflon remained wetted in the electrolyte tin solution, and that these water soluble solvents are all suitable

Example 14 (Surfactant Suitability For Wetting PTFE Powder)

To compare different surfactants, three separate mixtures were prepared:

- |    |    |   |       |
|----|----|---|-------|
| 5  | a) | Anionic surfactant                        |       |
|    |    | Teflon powder                             | 10 g  |
|    |    | Acetone                                   | 20 ml |
|    |    | Ethoxylated Sulfated Bisphenol A          | 1 g   |
|    | b) | Amphoteric surfactant                     |       |
| 10 |    | Teflon powder                             | 10 g  |
|    |    | Acetone                                   | 20 ml |
|    |    | Coco-imidazoline Dicarboxylic Sodium Salt | 1 g   |
|    | c) | Cationic surfactant                       |       |
|    |    | Teflon powder                             | 10 g  |
| 15 |    | Acetone                                   | 20 ml |
|    |    | Hexadecyltrimethylammoniumhydrogensulfate | 2 g   |

Each mixture was stirred to wet the teflon powder, then each added separately to one liter of the solution as of example 3. The results of a) showed that substantially all of the teflon was wetted (a small portion continued to float on top of the solution) and that for b) and c) the teflon remained wetted in the electrolyte tin solution, and that the anionic, amphoteric and cationic surfactants were all suitable as wetting agents.

solvent, the teflon remained wetted in the electrolyte tin solution, and that these water soluble solvents are all suitable

### Example 14 (Surfactant Suitability For Wetting PTFE Powder)

To compare different surfactants, three separate mixtures were prepared:

- |    |    |   |       |
|----|----|---|-------|
| 5  | a) | Anionic surfactant                        |       |
|    |    | Teflon powder                             | 10 g  |
|    |    | Acetone                                   | 20 ml |
|    |    | Ethoxylated Sulfated Bisphenol A          | 1 g   |
|    | b) | Amphoteric surfactant                     |       |
| 10 |    | Teflon powder                             | 10 g  |
|    |    | Acetone                                   | 20 ml |
|    |    | Coco-imidazoline Dicarboxylic Sodium Salt | 1 g   |
|    | c) | Cationic surfactant                       |       |
|    |    | Teflon powder                             | 10 g  |
| 15 |    | Acetone                                   | 20 ml |
|    |    | Hexadecyltrimethylammoniumhydrogensulfate | 2 g   |

Each mixture was stirred to wet the teflon powder, then each added separately to one liter of the solution as of example 3. The results of a) showed that substantially all of the teflon was wetted (a small portion continued to float on top of the solution) and that for b) and c) the teflon remained wetted in the electrolyte tin solution, and that the anionic, amphoteric and cationic surfactants were all suitable as wetting agents.

### Example 15 (Amount of Teflon)

To test the effect on the coefficient of friction of different amounts of teflon, separate solutions were prepared as in Example 3, but additionally containing 5 g/l, 10 g/l and 25 g/l of teflon. In each case, the teflon was prewetted with 20 ml acetone and 0.1 g nonylphenol ethoxylate.

Each of the above electrolytic bath solutions, and the solution of Example 3 without any teflon, as a control, were used to coat a coupon and the coefficient of friction of the coated coupon was measured as described above. The results of the measured coefficients of friction for Example 15 are presented in Fig. 6.

As shown by Fig. 6, there is a reduction of frictional coefficients caused by including codeposited teflon, at each amount, with 10 g/l giving the best result.

### Example 16 (Alternate Source of Teflon)

Du Pont supplies a PTFE powder suspended in water as a commercial product (ZONYL® PTFE Fluoropolymer Dispersion, TE 3667). The dispersion is reported to contain 58-62% PTFE, 0-5% octyl phenoxypolyethoxyethanol, 0-5% nonylphenoxypolyethoxyethanol, 33-42% water and < 0.5% ammonium perfluorooctanoate. The powder suspension in a plating bath is considerably more stable than the teflon which is wetted by using a solvent plus a surfactant as described here. The Du Pont teflon remains suspended and does not settle out, as is common with teflon that is not sufficiently wetted (and, after some time, even teflon wetted in accordance with the invention herein will settle). A test was run with the Du Pont suspended teflon. Example 5 was repeated, but with 10 g/l of Du Pont suspended teflon substituted for the 10 g/l teflon powder in 20 ml/l of acetone in example 5.

The above electrolytic bath solution was used to coat a coupon and the coefficient of friction of the coated coupon was measured as described above. The

### Example 15 (Amount of Teflon)

To test the effect on the coefficient of friction of different amounts of teflon, separate solutions were prepared as in Example 3, but additionally containing 5 g/l, 10 g/l and 25 g/l of teflon. In each case, the teflon was pretreated with 20 ml acetone and 0.1 g nonylphenol ethoxylate.

Each of the above electrolytic bath solutions, and the solution of Example 3 without any teflon, as a control, were used to coat a coupon and the coefficient of friction of the coated coupon was measured as described above. The results of the measured coefficients of friction for Example 15 are presented in Fig. 6.

As shown by Fig. 6, there is a reduction of frictional coefficients caused by including codeposited teflon, at each amount, with 10 g/l giving the best result.

### Example 16 (Alternate Source of Teflon)

Du Pont supplies a PTFE powder suspended in water as a commercial product (ZONYL® PTFE Fluoropolymer Dispersion, TE 3667). The dispersion is reported to contain 58-62% PTFE, 0-5% octyl phenoxypolyethoxyethanol, 0-5% nonylphenoxypolyethoxyethanol, 33-42% water and < 0.5% ammonium perfluorooctanoate. The powder suspension in a plating bath is considerably more stable than the teflon which is wetted by using a solvent plus a surfactant as described here. The Du Pont teflon remains suspended and does not settle out, as is common with teflon that is not sufficiently wetted (and, after some time, even teflon wetted in accordance with the invention herein will settle). A test was run with the Du Pont suspended teflon. Example 5 was repeated, but with 10 g/l of Du Pont suspended teflon substituted for the 10 g/l teflon powder in 20 ml/l of acetone in example 5.

The above electrolytic bath solution was used to coat a coupon and the coefficient of friction of the coated coupon was measured as described above. The



results of the measured coefficients of friction for Example 16 were essentially the same those of Example 5.

Example 17 (Surfactant/Additives)

5 a) A tin electroplating bath was prepared using the electroplating solution of Example 5, except that 1 g/l of ethoxylated sulfated bisphenol A (an anionic surfactant) was substituted for the two non-ionic surfactants of Example 5. Also, the Du Pont ZONYL<sup>®</sup> suspended teflon was used instead of teflon powder and acetone. All other conditions were the same as Example 5.

10 b) A tin electroplating bath was prepared using the electroplating solution of Example 5, except that 1 g/l of coco-imidazoline dicarboxylic sodium salt (an amphoteric surfactant) was substituted for the two non-ionic surfactants of Example 5. Also, the Du Pont suspended teflon was used instead of teflon powder and acetone. All other conditions were the same as Example 5.

15 c) A tin electroplating bath was prepared using the electroplating solution of Example 5, except that 2 g/l of hexadecyl trimethyl ammonium sulfate (a cationic surfactant) was substituted for the two non-ionic surfactants of Example 5. Also, the Du Pont suspended teflon was used instead of teflon powder and acetone. All other conditions were the same as Example 5.

20 The above electrolytic bath solutions were each used to coat a coupon and the coefficient of friction of the coated coupon was measured as described above. The results of the measured coefficients of friction for Example 17, in each case, were essentially the same as in Example 5.

Example 18 (Wear Test)

25 Using the solution of Example 5, steel bearings supplied by Delphi Chassis, a division of General Motors Corp. (GMC) were plated with a tin composite

results of the measured coefficients of friction for Example 16 were essentially the same those of Example 5.

Example 17 (Surfactant/Additives)

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10 b) A tin electroplating bath was prepared using the electroplating solution of Example 5, except that 1 g/l of coco-imidazoline dicarboxylic sodium salt (an amphoteric surfactant) was substituted for the two non-ionic surfactants of Example 5. Also, the Du Pont suspended teflon was used instead of teflon powder and acetone. All other conditions were the same as Example 5.

15 c) A tin electroplating bath was prepared using the electroplating solution of Example 5, except that 2 g/l of hexadecyl trimethyl ammonium sulfate (a cationic surfactant) was substituted for the two non-ionic surfactants of Example 5. Also, the Du Pont suspended teflon was used instead of teflon powder and acetone. All other conditions were the same as Example 5.

20 The above electrolytic bath solutions were each used to coat a coupon and the coefficient of friction of the coated coupon was measured as described above. The results of the measured coefficients of friction for Example 17, in each case, were essentially the same as in Example 5.

Example 18 (Wear Test)

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coating deposit to a thickness of 250 micro-inches, and other bearings were coated to a thickness of 500 micro-inches. The plated bearings were then tested by Delphi Chassis in an Underwood test machine specific for these tests. The test conditions were 3600 RPM, 7500 psi and the duration was 64 hours maximum.

5               Results showed that the above bearings survived the 64 hours load test with no failure. The disassembled bearings were inspected for wear and fatigue which were shown to be very light to light. This practical test indicated that the tin composite coating deposit in accordance with the invention was a very successful contact bearing surface.

10               The preferred tin deposits having the lowest coefficient of friction for a contact surface for bearings were determined to be those that include carbon in the form of an organic polymer or compound plus a solid lubricant, such as powdered teflon, graphite, or molybdenum disulfide in accordance with the invention. The coatings described herein were a suitable lead-free substitute for conventional 88:10:2  
15   lead:tin:copper coatings.

              It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the method and in the article set forth without departing from the spirit and scope of the invention, it is intended that all matter  
20   contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

              It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all

coating deposit to a thickness of 250 micro-inches, and other bearings were coated to a thickness of 500 micro-inches. The plated bearings were then tested by Delphi Chassis in an Underwood test machine specific for these tests. The test conditions were 3600 RPM, 7500 psi and the duration was 64 hours maximum.

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20   contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

              It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all



statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Particularly it is to be understood that in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such

5 ingredients wherever the sense permits.

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Particularly it is to be understood that in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such  
5 ingredients wherever the sense permits.

## C L A I M S

What is claimed is:

1. An engine bearing having a substantially lead free bearing surface coated on a substrate and suitable for frictional engagement with a second surface, the coated surface comprising: a tin layer deposited from a plating bath, the tin layer having codeposited solid lubricant and carbon compound inclusions, the coating being sufficiently durable, structured and well affixed to the substrate to serve as an engine bearing surface, the solid lubricant being selected and present in an effective amount to reduce the coefficient of friction of the surface without the presence of said lubricant and the carbon compound selected and proportioned to reduce the coefficient of friction and improve the plating properties of said surface, without said carbon source.
2. The engine bearing of claim 1, comprising an alloying element for forming an alloy with tin in sufficient amounts to change the properties of a coating which lacks the presence of such alloying element.
3. The engine bearing of claim 1, comprising at least one of copper and bismuth alloyed with the tin and in a lower percentage than the tin.
4. The engine bearing of claim 1, wherein said solid lubricant comprises PTFE.
5. The engine bearing of claim 1, wherein said solid lubricant comprises molybdenum disulfide.
6. The engine bearing of claim 1, wherein said solid lubricant comprises graphite.
7. The engine bearing of claim 1, wherein said carbon compound comprises an organic molecule or polymer deposited from a surface active additive grain refiner containing carbon in the plating bath used to plate said coating layer onto the substrate.

## CLAIMS

What is claimed is:

1. An engine bearing having a substantially lead free bearing surface coated on a substrate and suitable for frictional engagement with a second surface, the coated surface comprising: a tin layer deposited from a plating bath, the tin layer having codeposited solid lubricant and carbon compound inclusions, the coating being sufficiently durable, structured and well affixed to the substrate to serve as an engine bearing surface, the solid lubricant being selected and present in an effective amount to reduce the coefficient of friction of the surface without the presence of said lubricant and the carbon compound selected and proportioned to reduce the coefficient of friction and improve the plating properties of said surface, without said carbon source.
2. The engine bearing of claim 1, comprising an alloying element for forming an alloy with tin in sufficient amounts to change the properties of a coating which lacks the presence of such alloying element.
3. The engine bearing of claim 1, comprising at least one of copper and bismuth alloyed with the tin and in a lower percentage than the tin.
4. The engine bearing of claim 1, wherein said solid lubricant comprises PTFE.
5. The engine bearing of claim 1, wherein said solid lubricant comprises molybdenum disulfide.
6. The engine bearing of claim 1, wherein said solid lubricant comprises graphite.
7. The engine bearing of claim 1, wherein said carbon compound comprises an organic molecule or polymer deposited from a surface active additive grain refiner containing carbon in the plating bath used to plate said coating layer onto the substrate.

8. The engine bearing of claim 1, wherein said carbon compound comprises an organic molecule or polymer resulting from the presence of a brightener or grain refiner in the plating bath from which the coating was deposited.

9. The engine bearing of claim 1, wherein the carbon compound results from the presence of an ethoxylated alkyl-phenolic type surfactant in the plating bath.

10. The engine bearing of claim 1, wherein said carbon compound results from the presence of an aldehyde, selected from the group consisting of lower aliphatic aldehydes, aromatic aldehydes, heterocyclic aldehydes and combinations thereof, present in the plating bath from which the coating was deposited.

11. The engine bearing of claim 1, wherein the carbon compound is deposited from bisphenol A ethoxylate present in the plating bath.

12. The engine bearing of claim 1, wherein the carbon compound is deposited from nonylphenol ethoxylate present in the plating bath.

13. The engine bearing of claim 1, wherein the carbon compound is deposited from ethoxylate sulfated bisphenol A present in the plating bath.

14. The engine bearing of claim 1, wherein said carbon compound is deposited from a soluble surface active additive containing carbon which is at least one soluble surface active additive containing carbon which acts as a grain refiner or brightener, selected from the group consisting of non-ionic surfactants containing higher alcohols condensed with alkylene oxide groups, amphoteric surfactants and anionic surfactants.

15. The engine bearing of claim 1, wherein said carbon compound is deposited from a soluble surface active additive containing higher alcohols condensed with alkylene oxide groups, and wherein said higher alcohols are at least one higher alcohol selected from the group consisting of aliphatic alcohols, aromatic alcohols, and heterocyclic alcohols.

16. The engine bearing of claim 1, wherein said carbon compound is deposited from a non-ionic surfactant which acts as a brightener or grain refiner containing higher alcohols condensed with alkylene oxide groups are at least one

8. The engine bearing of claim 1, wherein said carbon compound comprises an organic molecule or polymer resulting from the presence of a brightener or grain refiner in the plating bath from which the coating was deposited.

9. The engine bearing of claim 1, wherein the carbon compound results from the presence of an ethoxylated alkyl-phenolic type surfactant in the plating bath.

10. The engine bearing of claim 1, wherein said carbon compound results from the presence of an aldehyde, selected from the group consisting of lower aliphatic aldehydes, aromatic aldehydes, heterocyclic aldehydes and combinations thereof, present in the plating bath from which the coating was deposited.

11. The engine bearing of claim 1, wherein the carbon compound is deposited from bisphenol A ethoxylate present in the plating bath.

12. The engine bearing of claim 1, wherein the carbon compound is deposited from nonylphenol ethoxylate present in the plating bath.

13. The engine bearing of claim 1, wherein the carbon compound is deposited from ethoxylate sulfated bisphenol A present in the plating bath.

14. The engine bearing of claim 1, wherein said carbon compound is deposited from a soluble surface active additive containing carbon which is at least one soluble surface active additive containing carbon which acts as a grain refiner or brightener, selected from the group consisting of non-ionic surfactants containing higher alcohols condensed with alkylene oxide groups, amphoteric surfactants and anionic surfactants.

15. The engine bearing of claim 1, wherein said carbon compound is deposited from a soluble surface active additive containing higher alcohols condensed with alkylene oxide groups, and wherein said higher alcohols are at least one higher alcohol selected from the group consisting of aliphatic alcohols, aromatic alcohols, and heterocyclic alcohols.

16. The engine bearing of claim 1, wherein said carbon compound is deposited from a non-ionic surfactant which acts as a brightener or grain refiner containing higher alcohols condensed with alkylene oxide groups are at least one

alkylene oxide group selected from the group consisting of ethylene oxide and propylene oxide.

17. The engine bearing of claim 1, wherein said carbon source is deposited from a soluble surface active additive containing carbon which is a non-ionic surfactant which acts as a grain refiner or brightener, containing higher alcohols in which the terminal hydroxide group has been modified to include a solubilizing group condensed with alkylene oxide groups, and wherein said solubilizing group is at least one solubilizing group selected from the group consisting of halides, amines, sulfates, sulfonates, phosphates and phosphonates.

18. A bearing having a substantially lead free bearing surface coated on a substrate and suitable for frictional engagement with a second surface, the coated surface having sufficient durability to withstand at least 64 hours of wear at least 7500 psi and a speed of 3600 RPM and exhibit substantially no wear, the coated surface comprising: a tin layer deposited from a plating bath, the tin layer having codeposited solid lubricant and carbon compound inclusions, the solid lubricant being selected and present in an effective amount to reduce the coefficient of friction of the surface without the presence of said lubricant and the carbon compound selected and proportioned to reduce the coefficient of friction and improve the plating properties of said surface, without said carbon source.

19. The engine bearing of claim 18, wherein said solid lubricant comprises PTFE.

20. The engine bearing of claim 18, wherein said solid lubricant comprises molybdenum disulfide.

21. The engine bearing of claim 18, wherein said solid lubricant comprises graphite.

22. The engine bearing of claim 18, wherein said carbon compound comprises an organic molecule or polymer deposited from a surface active additive grain refiner or brightener containing carbon in the plating bath used to plate said coating layer onto the substrate.

alkylene oxide group selected from the group consisting of ethylene oxide and propylene oxide.

17. The engine bearing of claim 1, wherein said carbon source is deposited from a soluble surface active additive containing carbon which is a non-ionic surfactant which acts as a grain refiner or brightener, containing higher alcohols in which the terminal hydroxide group has been modified to include a solubilizing group condensed with alkylene oxide groups, and wherein said solubilizing group is at least one solubilizing group selected from the group consisting of halides, amines, sulfates, sulfonates, phosphates and phosphonates.

18. A bearing having a substantially lead free bearing surface coated on a substrate and suitable for frictional engagement with a second surface, the coated surface having sufficient durability to withstand at least 64 hours of wear at least 7500 psi and a speed of 3600 RPM and exhibit substantially no wear, the coated surface comprising: a tin layer deposited from a plating bath, the tin layer having codeposited solid lubricant and carbon compound inclusions, the solid lubricant being selected and present in an effective amount to reduce the coefficient of friction of the surface without the presence of said lubricant and the carbon compound selected and proportioned to reduce the coefficient of friction and improve the plating properties of said surface, without said carbon source.

19. The engine bearing of claim 18, wherein said solid lubricant comprises PTFE.

20. The engine bearing of claim 18, wherein said solid lubricant comprises molybdenum disulfide.

21. The engine bearing of claim 18, wherein said solid lubricant comprises graphite.

22. The engine bearing of claim 18, wherein said carbon compound comprises an organic molecule or polymer deposited from a surface active additive grain refiner or brightener containing carbon in the plating bath used to plate said coating layer onto the substrate.



23. The engine bearing of claim 18, wherein the carbon compound results from the presence of an ethoxylated alkyl-phenolic type surfactant in the plating bath.

24. The engine bearing of claim 18, wherein said carbon compound results from the presence of an aldehyde, selected from the group consisting of lower aliphatic aldehydes, aromatic aldehydes, heterocyclic aldehydes and combinations thereof, present in the plating bath from which the coating was deposited.

25. The engine bearing of claim 18, wherein the carbon compound is deposited from bisphenol A ethoxylate present in the plating bath.

26. The engine bearing of claim 18, wherein the carbon compound is deposited from nonylphenol ethoxylate present in the plating bath.

27. The engine bearing of claim 1, wherein the carbon compound is deposited from ethoxylate sulfated bisphenol A present in the plating bath.

23. The engine bearing of claim 18, wherein the carbon compound results from the presence of an ethoxylated alkyl-phenolic type surfactant in the plating bath.

24. The engine bearing of claim 18, wherein said carbon compound results from the presence of an aldehyde, selected from the group consisting of lower aliphatic aldehydes, aromatic aldehydes, heterocyclic aldehydes and combinations thereof, present in the plating bath from which the coating was deposited.

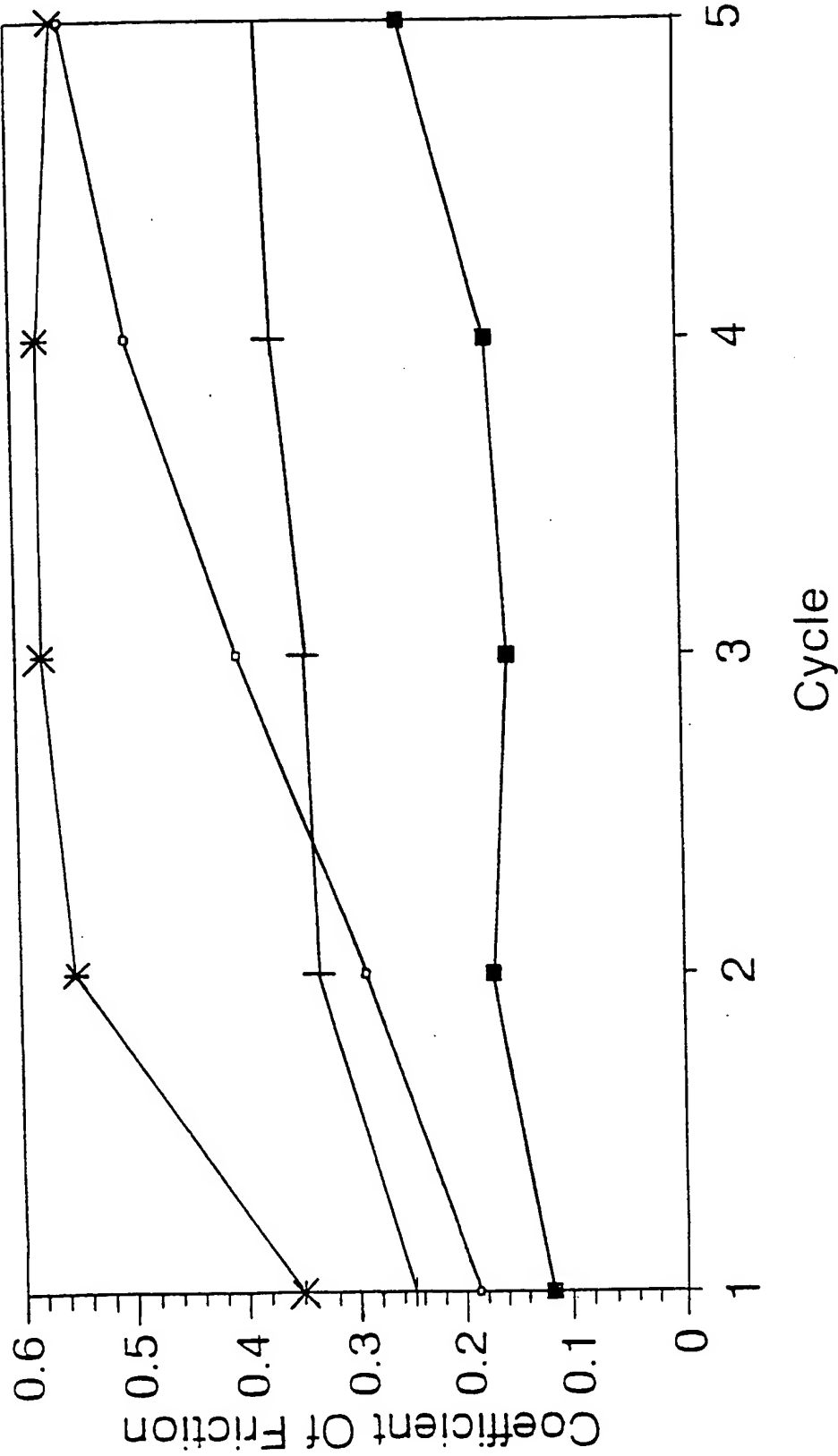
25. The engine bearing of claim 18, wherein the carbon compound is deposited from bisphenol A ethoxylate present in the plating bath.

26. The engine bearing of claim 18, wherein the carbon compound is deposited from nonylphenol ethoxylate present in the plating bath.

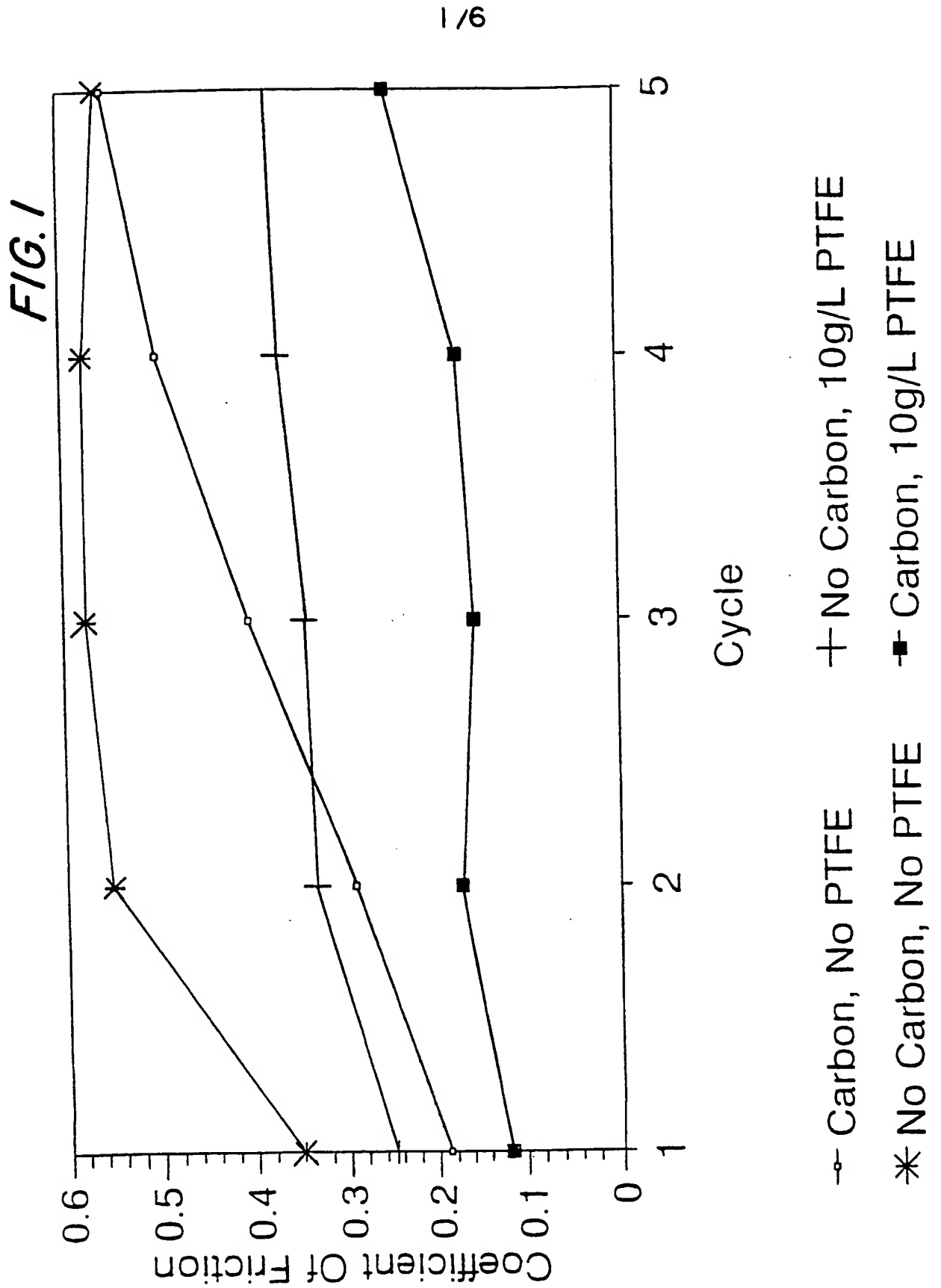
27. The engine bearing of claim 1, wherein the carbon compound is deposited from ethoxylate sulfated bisphenol A present in the plating bath.

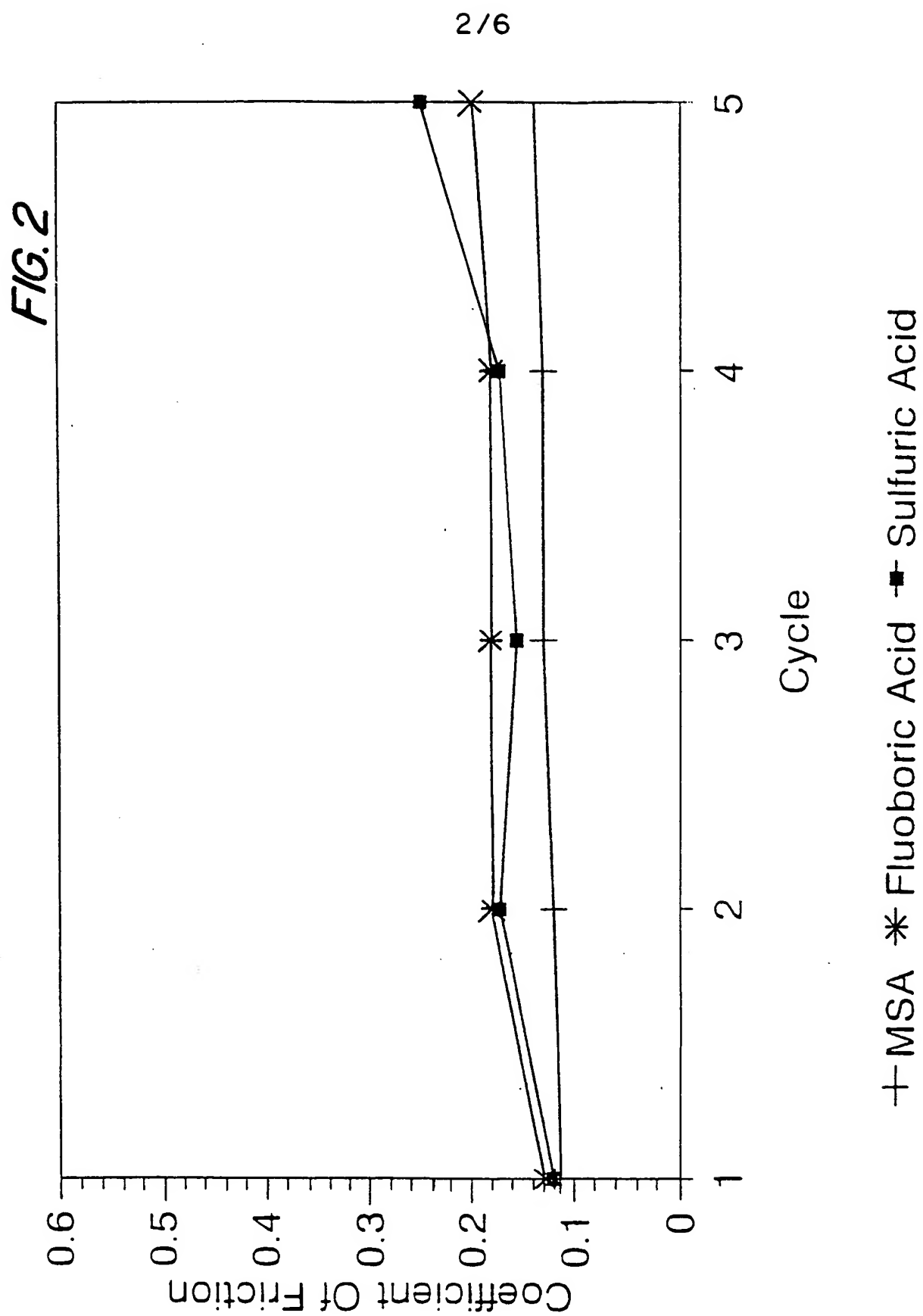
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FIG. 1



○ Carbon, No PTFE    + No Carbon, 10g/L PTFE  
 \* No Carbon, No PTFE    ■ Carbon, 10g/L PTFE





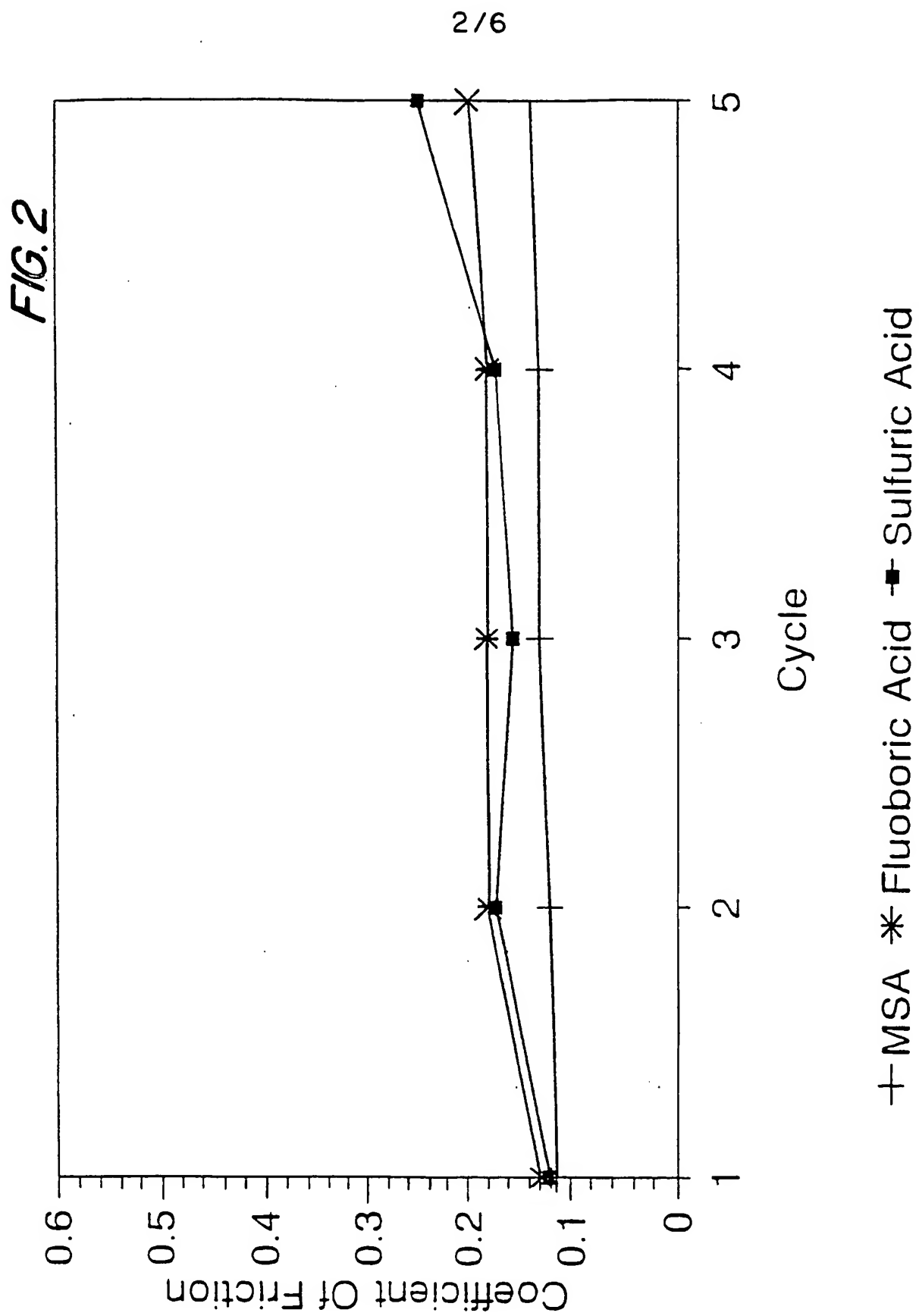
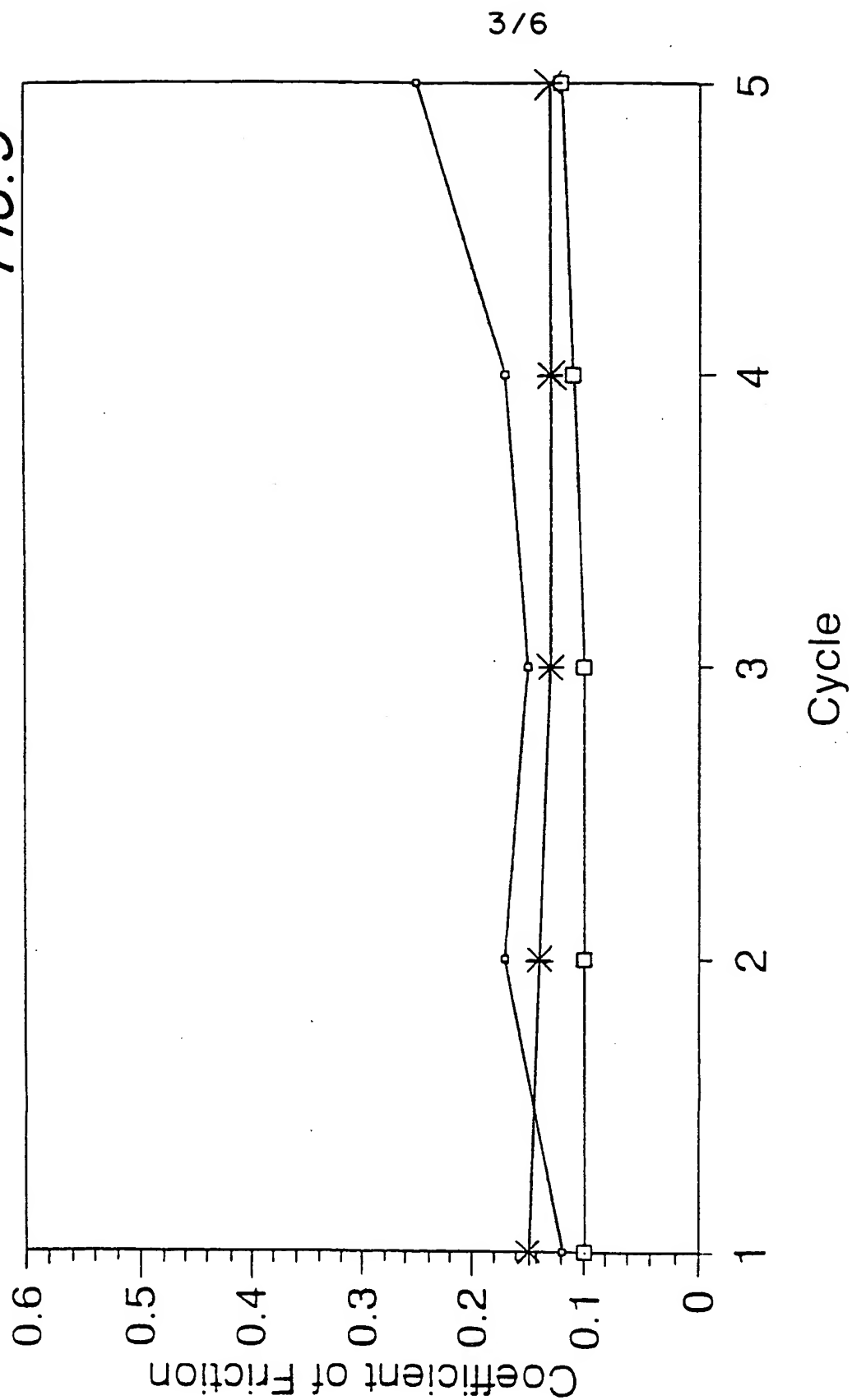
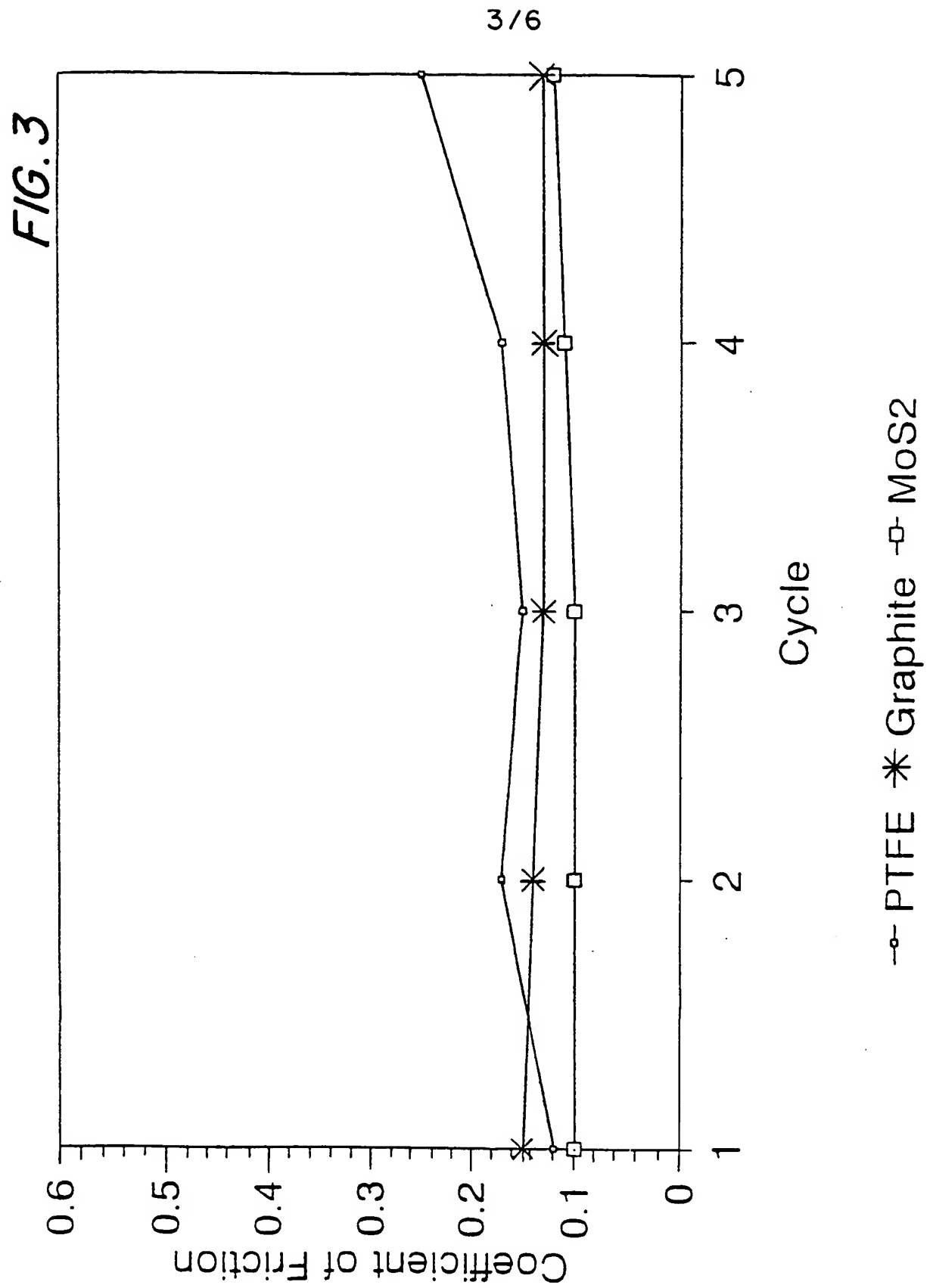


FIG. 3



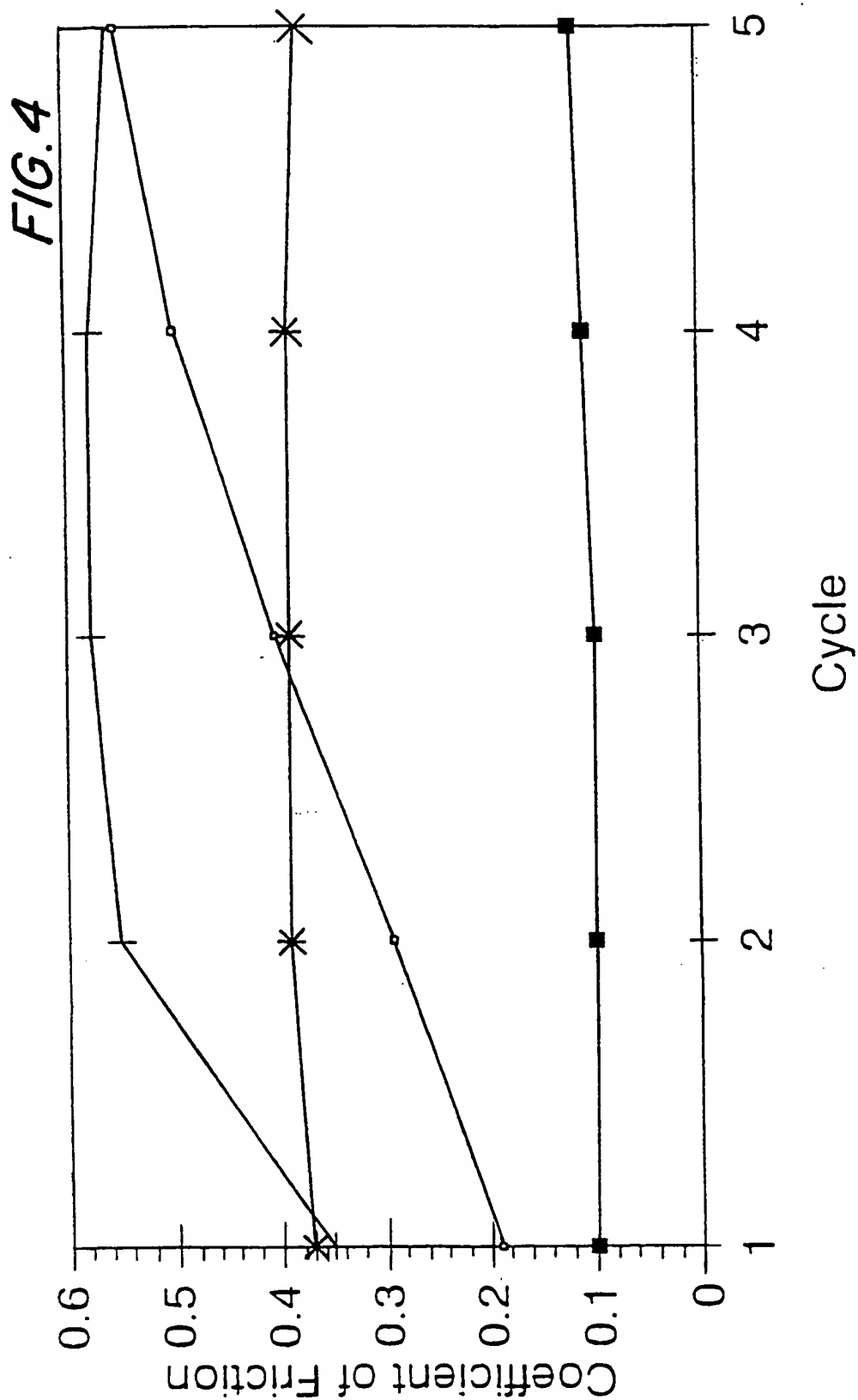
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-□- PTFE \* Graphite -○- MoS2



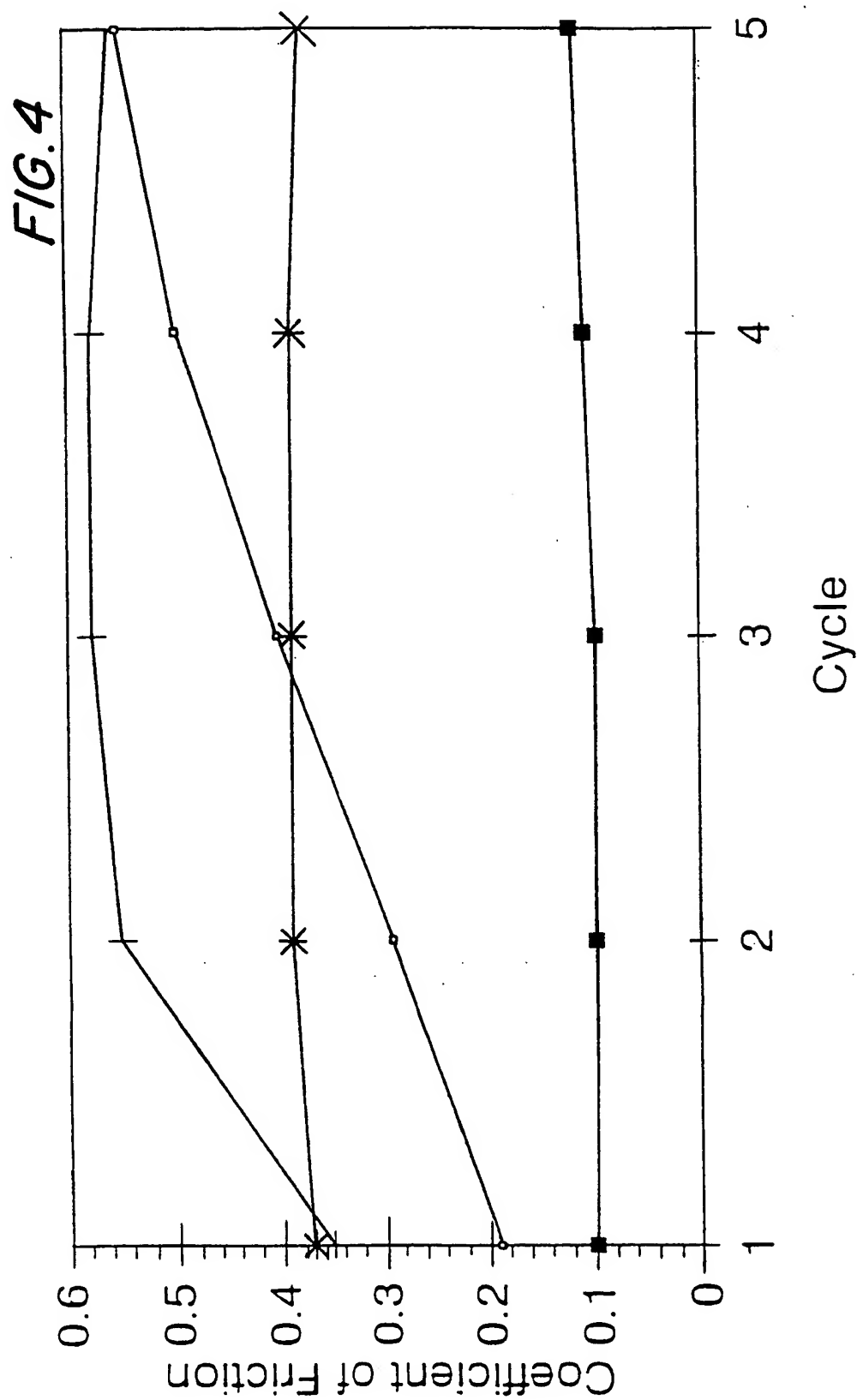


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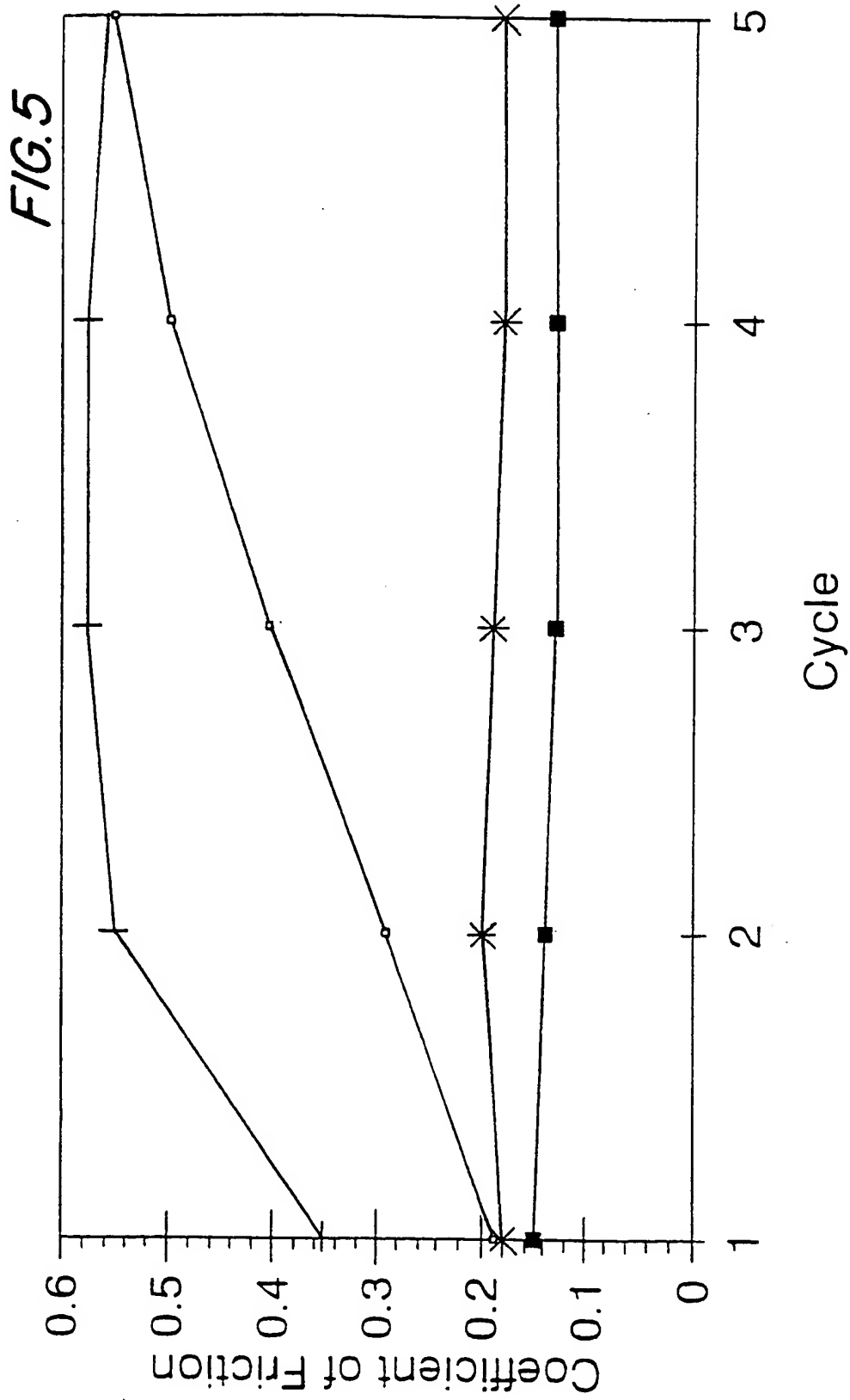


○ Carbon, no MoS2    + No Carbon, no MoS2  
\* No Carbon, 10 g/L MoS2    ■ Carbon, 10 g/L MoS2

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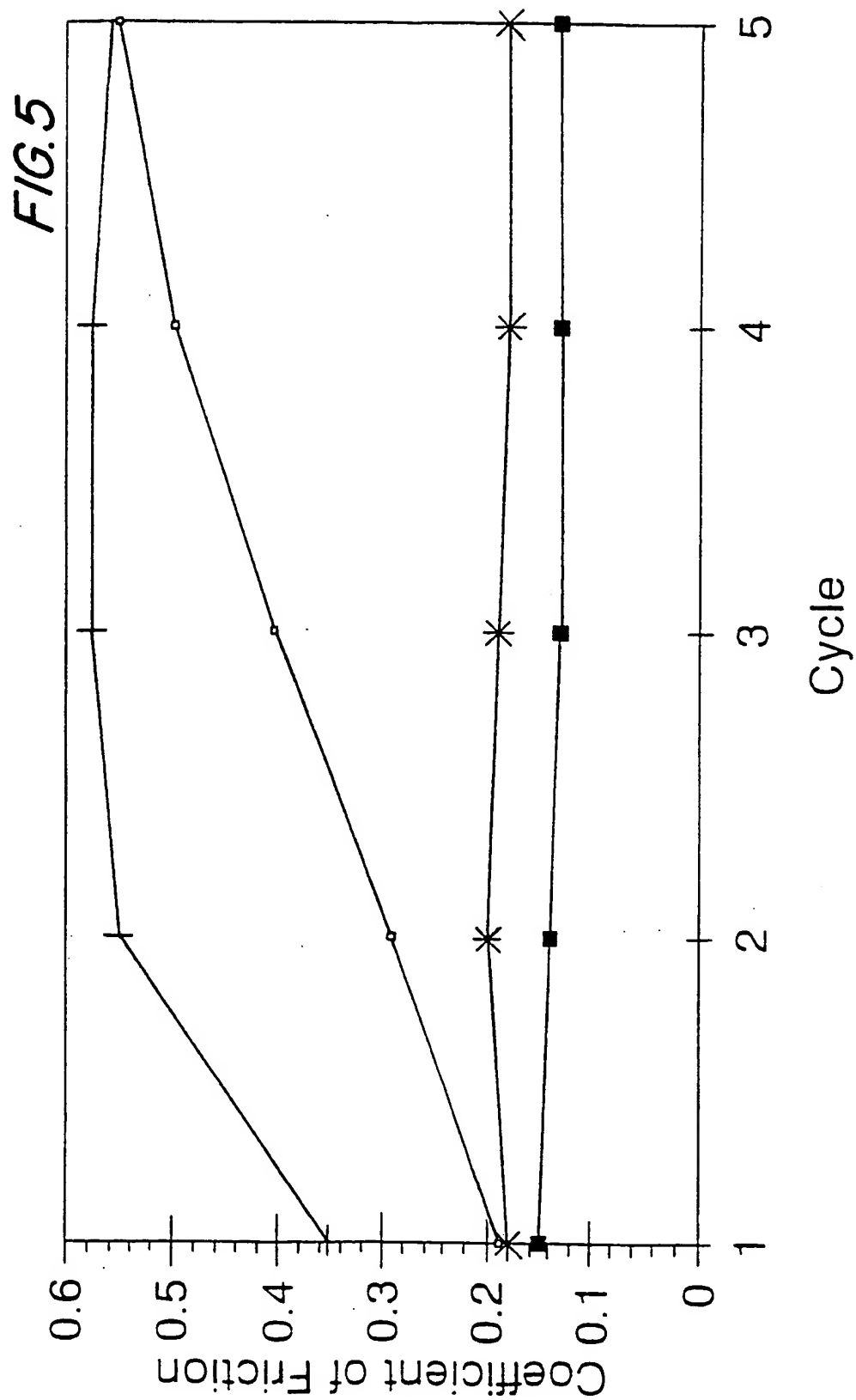


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○ Carbon, no Graphite    + no Carbon, no Graphite  
 \* no Carbon, 10g/L Graphite    ■ Carbon, 10g/L Graphite

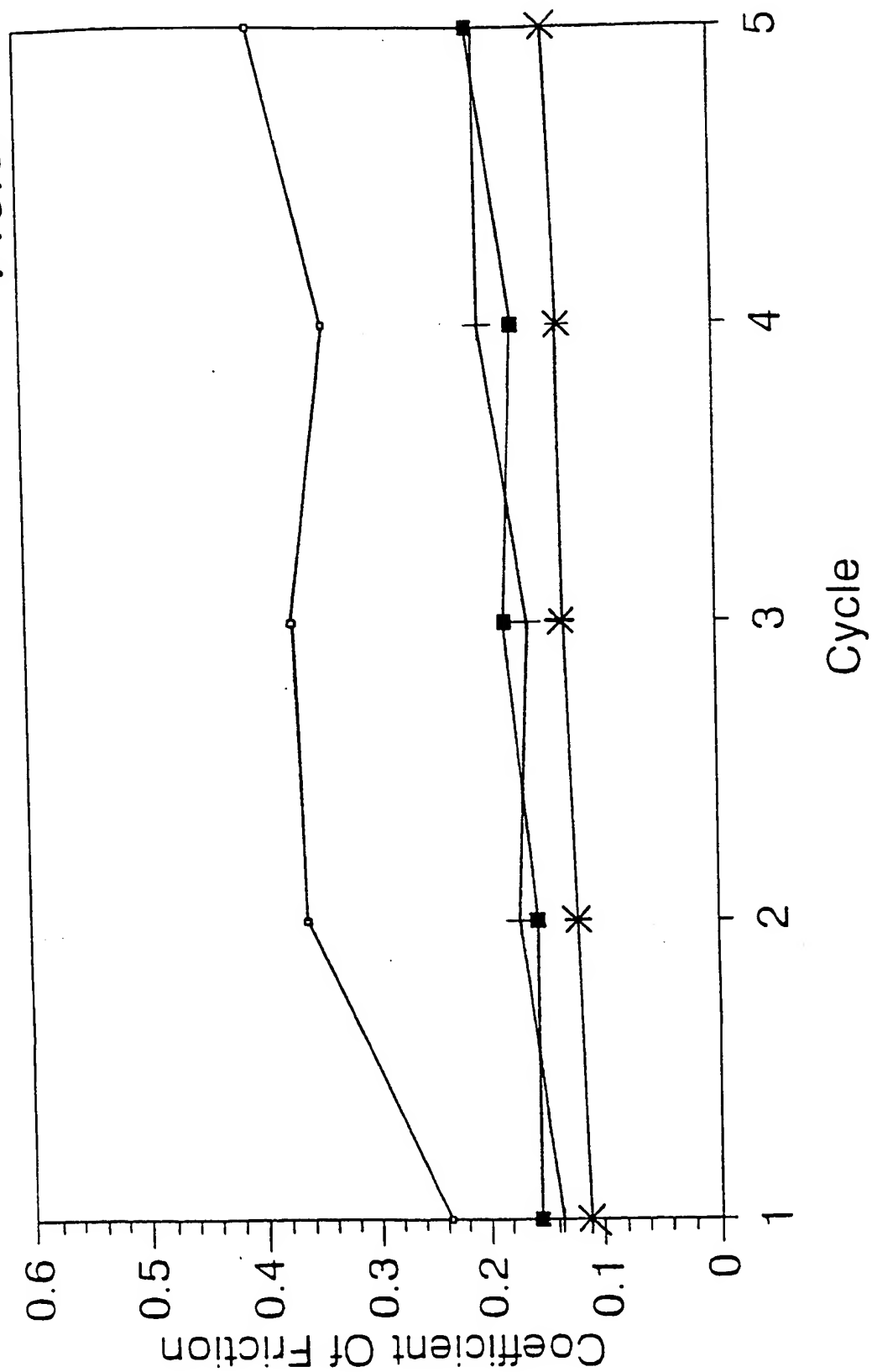
5/6



○ Carbon, no Graphite    + no Carbon, no Graphite  
\* no Carbon, 10g/L Graphite    ■ Carbon, 10g/L Graphite

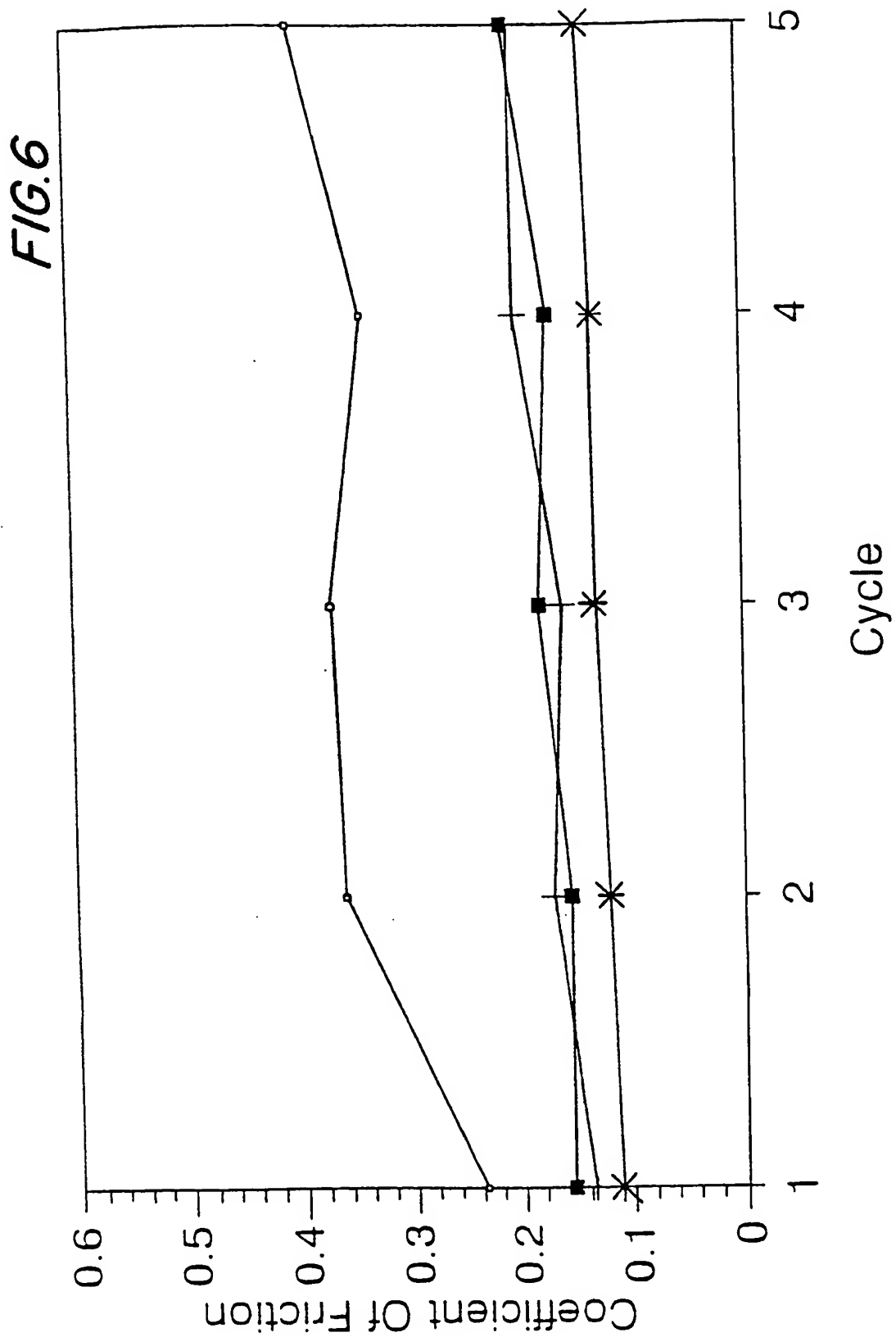
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FIG. 6



—○— 0g/L PTFE —\*— 10g/L PTFE —■— 25g/L PTFE

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—○— 0g/L PTFE + 5g/L PTFE \* 10g/L PTFE —■— 25g/L PTFE

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/21957

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 15/00; C25D 3/30.

US CL :428/646; 935; 205/109,253,254; 384/912.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/646; 935; 205/109,253,254; 384/912.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; STN/CHEMICAL ABSTRACT.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACT 1993:41977	1-27.
Y	US 3,787,294 A (KUROSAKI et al.) 22 January 1974, see abstract; col. 2, lines 44-51; col. 3, lines 52-59; col. 4, lines 52-59; and Examples 3-4.	1-27.
Y	US 4,994,155 A (TOBEN et al.) 19 February 1991, col. 3, line 52 through col. 4, line 19; col. 5, line 20 through col. 6, line 2; and col. 6, lines 15-22.	1-27

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

12 FEBRUARY 1998

Date of mailing of the international search report

26 FEB 1998

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
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## INTERNATIONAL SEARCH REPORT

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later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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\*Y\*

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*A\*

document member of the same patent family

Date of the actual completion of the international search

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